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(54) Title: WATERPROOFING ADDITIVE FOR CEMENT AND CONCRETE COMPRISING MODIFIED POZZOLANIC MATERIALS		
(57) Abstract A waterproofing additive for cement and/or concrete comprising a pozzolanic material (such as silica fume, refined natural microsilica or metakaolin) modified with a hydrophobic material (such as butyl stearate, calcium stearate, oleic acid or a silicon emulsion).		

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WATERPROOFING ADDITIVE FOR CEMENT AND CONCRETE
COMPRISING MODIFIED POZZOLANIC MATERIALS

Waterproofing is one of the most critical issues for the durability of concrete. The majority of concrete failures are attributed to the high permeability and sorptivity of concrete against water penetration and the ingress of chloride or sulfate ions dissolved in the water, causing not only water leakage but also the corrosion of steel rebars and destructive expansion of the concrete.

Silica fume, a by-product from the production of silicon or ferro-silicon alloys, is commonly used as a cement and concrete additive to produce corrosion-resistant concrete, concrete having improved mechanical properties or water-tight concrete (see, for example, US 4,118,242, US 4,310,486 and US 5,472,501). However, its disadvantages are poor workability and relatively high surface water absorption due to the capillary action of fine capillary pores which result in high sorptivity of the concrete and therefore potential high chloride/sulfate build up at the splash and tidal zones of marine concrete structures. Furthermore, the high water absorption will result in a concrete which is water-tight but not damp-proof and will fail to meet the commonly used project specification of a water absorption of less than 1% of the concrete when it is tested in accordance with BS1881 : Part 122.

Hydrophobic compounds, such as calcium stearate, silicon, wax or bitumen emulsion are also commonly used as waterproofing admixtures of concrete, to impart a hydrophobic coating to the capillary surfaces as well as blocking some pores. However such compounds have the disadvantages of reduced compressive strength (typically 10-15% lower than the plain concrete) and reduced effectiveness under high hydrostatic head.

Therefore, for a durable waterproofing concrete both low permeability and low absorption to water are sought. One solution is to make separate additions of silica fume and hydrophobic compound during the production of the concrete. However, this requires additional mixing/dispersing and the hydrophobic compound is usually

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added as an emulsion in order to achieve a homogeneous mix. The pre-emulsifying of the hydrophobic compound and the complicated dosing procedure make such a procedure impractical and uneconomical for use on construction sites. It should also be noted that the emulsion can only have limited use in cold environments because it is generally not frost resistant. Furthermore, the emulsifier may reduce the hydrophobic action and cause excessive air entrainment and loss of strength.

Another approach is disclosed in US 4,762,867. This describes the use of an amphiphilic synthetic polymer dispersion to reduce water absorption in cement mortar and concrete. Synthetic polymer dispersion is very expensive and has an adverse effect on the compressive strength of the concrete. It is not practical and has only limited usage. It is therefore not generally used by the construction industry for large scale waterproofing concrete production.

According to the present invention from one aspect there is provided a waterproofing additive for cement and/or concrete, comprising at least one pozzolanic material modified with at least one hydrophobic material.

The pozzolanic material preferably comprises one or more pozzolanic components. The pozzolanic material preferably comprises one or more of silica fume, microsilica and metakaolin. The silica fume may be densified or undensified silica fume. The microsilica is preferably refined natural microsilica and is preferably amorphous. One particularly preferred composition for the pozzolanic material is a mixture of silica fume and microsilica, most preferably in approximately equal amounts by weight.

The hydrophobic material is suitably a hydrophobic compound, preferably an organic or organometallic compound, most preferably of a long chain paraffinic acid. The hydrophobic material may be a paraffinic or fatty acid ester, e.g. butyl stearate. The hydrophobic compound may be a soap, especially a metallic soap of a paraffinic acid, e.g. calcium stearate, magnesium stearate or aluminium stearate, or an organic soap of a paraffinic acid, e.g. an ammonium salt. The hydrophobic compound may be oleic acid, a wax emulsion, siloxane or a silicon emulsion.

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The or each pozzolanic constituent of the additive may be modified with one or more hydrophobic materials. Preferred waterproofing additives are mixtures of at least one pozzolanic material (e.g. silica fume, microsilica or metakaolin) with at least one hydrophobic compound, or possibly two or more hydrophobic compounds of different types. The combination of such materials has been observed to enable better mixing and a freer flowing powder nature of the finished product, as well as increased shelf life thereof.

The pozzolanic material is preferably modified by spraying and/or blending with the hydrophobic material, suitably in a high speed/shear mixer. The mixing operation preferably results in an intimate, and preferably substantially fully mixed, mixture of the pozzolanic material and the hydrophobic material(s).

The total weight of the hydrophobic material(s) in the waterproofing additive is suitably in the range from 5 to 30% of the weight of the pozzolanic material, preferably 5 to 15% and most preferably around 10%.

A particularly preferred composition is an approximately 1:1 mixture (by weight) of densified silica fume and microsilica modified with approximately 10% (by weight of the combined pozzolanic constituents) of butyl stearate. Another particularly preferred composition is metakaolin modified with approximately 10% (by weight) of butyl stearate.

According to a second aspect of the present invention there is provided a cement mortar or concrete comprising a waterproofing additive according to the first aspect of the invention. The cement mortar or concrete preferably comprises an amount of the waterproofing additive such that the pozzolanic material of the additive is present in the cement mortar or concrete in an amount in the range from 5 to 15% of the weight of cement, and most preferably from around 8 to 10%. The cement mortar or concrete preferably has improved water impermeability (suitably less than 10 mm after 28 days when measured in accordance with DIN 1048) and/or reduced water absorption (suitably less than 1% when measured in accordance with BS1881 : Part 122), preferably whilst retaining acceptable compressive strength. Thus, the

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waterproofing additive is preferably capable of acting to improve the waterproofing of cement mortar and/or concrete.

According to a third aspect of the present invention there is provided a method of preparing a waterproofing additive for cement and/or concrete, comprising modifying a pozzolanic material by spraying and/or blending with a hydrophobic material. The step of spraying and/or blending is performed using a high speed/shear mixer.

According to a fourth aspect of the present invention there is provided a method of preparing cement mortar or concrete comprising mixing cement, sand and water with a waterproofing additive according to the first aspect of the invention and/or manufactured in accordance with the third aspect of the invention.

In ASTM C618, a pozzolan is defined as a siliceous and aluminous material which, in itself, possesses little or no cementitious value but which will, in finely divided form in the presence of moisture, react chemically with calcium hydroxide at ordinary temperature to form compounds possessing cementitious properties.

The present invention will now be described by way of example only, with reference to the following embodiments which are illustrative and not limiting.

EXAMPLE 1 - Waterproofing for Cement Mortars

The mixture proportions of the cement mortars in this example are based on the following composition: cement (OPC) : water : sand : waterproofing additive : liquid superplasticizer in the ratio of 1 : 0.38 : 2.61 : 0-0.08 : 0.01-0.02 (by weight) respectively. The waterproofing additive comprises a pozzolanic material (e.g. silica fume, refined natural microsilica or metakaolin) modified with a hydrophobic material (e.g. an organic or organometallic compound such as butyl stearate, calcium stearate, another metallic soap of a paraffinic acid, oleic acid, wax emulsion, siloxane or a silicon emulsion). Thus, in the waterproofing additive the hydrophobic compound(s) are provided integrally with the pozzolanic material.

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The silica fume that was used was a commercially available product having a typical composition as shown in table 1 (with constituents indicated by weight in %):

Table 1: Typical Composition of Silica Fume

Composition	SiO ₂	SO ₃	C	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O
Usual range	85-95	0.1-0.5	1.0-6.0	0.1-0.4	0.1-0.5	0.1-1.0	0.1-1.0	0.1-1.0
Typical	90-94	1.0 max	3.0 max	0.3	0.3	0.4	1.0 max	1.0 max

Both densified silica fume (as supplied by Scancern Materials Pty Ltd, Australia) and undensified silica fume (as supplied by Elkem Materials, Norway) are suitable. The typical density range for the densified silica fume is 500-650 kg/m³ and for undensified silica fume is 250-400 kg/m³.

The microsilica that was used was a refined natural amorphous silica (as supplied by Microsilica New Zealand Limited, New Zealand). The typical composition is given in table 2 (with constituents indicated by weight in %):

Table 2: Typical Composition of Refined Natural Microsilica

Composition	SiO ₂	SO ₃	Cl	LOI	Alkali content	Bulk Density
Typical	90.8	0.15	0.001	2.2	0.012	700kg/m ³

The metakaolin that was used was a commercially available product produced by high temperature treatment of kaolin (as supplied by ECC International, UK or Engelhard Corporation, USA). The typical composition is given in table 3 (with constituents indicated by weight in %):

Table 3: Typical Composition of Metakaolin

Composition	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O
Typical	52-55	40-42	0.6-4.6	0-0.1	0.2-0.4	0.6-2.4	<0.1

The selected pozzolanic materials were processed by spraying and blending with one

or more hydrophobic compounds in a high speed, high shear mixer to produce a surface modified waterproofing additive for cement and concrete. The preferred hydrophobic compounds are butyl stearate, calcium stearate or other metallic soaps of paraffinic acids which are commonly used as waterproofing additives in the cement and concrete. Other suitable hydrophobic compounds include oleic acid, wax emulsion, siloxane and silicon emulsions, but with reduced effectiveness.

Cement mortar mixtures in which a range of hydrophobically modified pozzolanic materials with cement, sand, water and superplasticizer were prepared in a Hobart mixer. The liquid superplasticizer was added to adjust the mix to a constant workability (flow). The mortars' compressive strengths were tested according to ASTM C109 and the water absorption was tested by a modified method according to BS 1881 : Part 122 at 7 days. The results (including results for a control sample with none of the hydrophobic material) are summarized for each of the chosen pozzolanic materials in tables 4, 5, 6 and 7.

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Table 4: Test Results of Cement Mortar with Modified Densified Silica Fume

Hydrophobic	Butyl		Calcium	Oleic	Wax	Silicon	
Compound	None	Stearate	Stearate	Acid	Emulsion	Siloxane	Emulsion
Compressive							
Strength (MPa)							
@ 1 day	36.0	35.0	31.0	24.0	24.5	17.5	7.0
@ 7 days	63.5	63.0	54.0	52.0	49.0	52.5	46.0
@ 28 days	68.5	70.5	61.5	70.0	64.5	71.0	74.0
Water absorption @ 7 days							
(%)	2.20	0.58	0.68	1.94	1.56	1.55	2.09

Table 5: Test Results of Cement Mortar with Modified Undensified Silica Fume

Hydrophobic	Butyl		Calcium	Oleic	Wax	Silicon	
Compound	None	Stearate	Stearate	Acid	Emulsion	Siloxane	Emulsion
Compressive							
Strength (MPa)							
@ 1 day	36.0	34.5	31.0	30.0	35.0	7.0	3.0
@ 7 days	63.5	68.5	60.0	66.5	66.0	62.0	66.0
@ 28 days	68.5	72.0	66.0	70.0	69.5	75.0	74.0
Water absorption @ 7 days							
(%)	2.20	0.65	0.80	1.41	1.46	1.43	1.69

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Table 6: Test Results of Cement Mortar with Modified Microsilica

Hydrophobic Compound	None	Butyl Stearate	Calcium Stearate	Oleic Acid	Wax Emulsion	Silicon Siloxane	Emulsion
Compressive Strength (MPa)							
@ 1 day	38.0	36.0	35.5	29.5	33.0	1.5	12.0
@ 7 days	66.5	63.0	59.5	54.5	62.0	43.5	54.0
@ 28 days	76.0	78.0	73.0	79.0	71.0	73.5	76.5
Water absorption @ 7 days (%)	2.12	0.63	0.79	1.61	1.70	1.43	2.04

Table 7: Test Results of Cement Mortar with Modified Metakaolin

Hydrophobic Compound	None	Butyl Stearate	Calcium Stearate	Oleic Acid	Wax Emulsion	Silicon Siloxane	Emulsion
Compressive Strength (MPa)							
@ 1 day	33.0	32.0	30.5	33.0	33.0	1.0	2.5
@ 7 days	62.5	63.0	64.0	65.0	64.0	60.5	56.0
@ 28 days	65.0	67.5	64.0	71.0	68.0	71.0	72.0
Water absorption @ 7 days (%)	2.30	0.58	0.63	1.29	1.42	1.53	1.66

The above study shows that the waterproofing additive can effectively reduce the water absorption of the cement while generally no or little adverse effect on the 28 days compressive strength was observed. In fact, in many cases increased compressive strength was observed. The fluctuation in the strength data of the plain

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mortars was due to the different sources of cement available at the different times of testing. Therefore comparison should be restricted to within each group of tests. Pozzolans modified with butyl stearate showed the best combined performance in term of strength development and water absorption.

Similar mortars could be prepared using a mixture of more than one waterproofing additive. More than one pozzolanic material could be used, and the or each pozzolanic material could be modified with the same or different hydrophobic materials or with more than one hydrophobic material.

EXAMPLE 2 - Waterproofing for Concrete

The effectiveness of the waterproofing additive on concrete is demonstrated by the following study.

The modified pozzolanic material employed in this study was densified silica fume (as described in detail in relation to example 1) modified with 10% butyl stearate. Other pozzolanic materials modified with butyl stearate are expected to perform similar or better as shown in the cement mortar studies. Two typical water to cement (w/c) ratios of 0.36 and 0.45 were used in this study and the dosage levels of the modified silica fume (MSF) were at 5% and 10% by weight of the total binder (cement + silica fume) content. The concrete mixture proportions and the test results are shown in tables 8 and 9, one table for each of the water : cement ratios..

The concretes were prepared in a concrete drum mixer. The cement (OPC), densified silica fume and the liquid superplasticizer (high range water reducing agent: HRWRA) were commercially available materials. The fresh properties and strength of the concrete were tested according to the guidelines set in BS 1881. The water absorption was tested at 7 and 28 days in accordance with BS 1881 : Part 122. The water penetration was tested at 28 days according to DIN 1048 and the rapid chloride penetration test was carried out at 28 days according to ASTM 1202.

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Table 8: Test Results of Concrete (water : cement=0.36)

Materials	Plain (no MSF)	MSF-1 at 5%	MSF-2 at 10%
Mixture Proportion			
OPC (kg)	420	399	378
Sand (kg)	786	786	786
Stone (kg)	1063	1063	1063
Water (kg)	151	151	151
Modified Silica Fume (kg)	-	21	42
HRWRA (L/100 kg Binder)	1.2	1.3	2.0
Results			
Initial Slump (mm)	155	200	200
Initial Setting Time (hrs:min)	7:45	Not tested	11:00
Final Setting Time (hrs:min)	9:35	Not tested	13:15
Compressive Strength (MPa)			
@ 1 day	47.0	35.5	30.0
@ 3 days	64.0	58.0	53.0
@ 7 days	72.5	70.0	68.5
@ 28 days	76.0	79.0	78.0
@ 56 days	78.5	84.0	82.0
Water absorption (%)			
@ 7 days	1.83	0.86	0.65
@ 28 days	1.80	0.76	0.59
Water penetration			
@ 28 days (mm)	15.0	3.0	1.0
Rapid Chloride Penetration			
@ 28 days (Coulombs)	2889	1130	479

Table 9: Test Results of Concrete (water : cement = 0.45)

Materials	Plain (no MSF)	MSF-1 at 5%	MSF-2 at 10%
Mixture Proportion			
OPC (kg)	380	361	342
Sand (kg)	782	782	782
Stone (kg)	1057	1057	1057
Water (kg)	171	171	171
Modified Silica Fume (kg)	-	19	38
HRWRA (L/100 kg Binder)	0.9	1.2	1.4
Results			
Initial Slump (mm)	130	140	105
Initial Setting Time (hrs:min)	5:30	5:25	6:00
Final Setting Time (hrs:min)	6:45	7:00	7:25
Compressive Strength (MPa)			
@ 1 day	32.5	31.5	27.0
@ 3 days	49.5	47.0	44.0
@ 7 days	57.0	57.5	56.5
@ 28 days	65.0	68.0	64.5
@ 56 days	65.5	70.0	69.5
Water absorption (%)			
@ 7 days	2.28	1.02	0.78
@ 28 days	2.20	0.99	0.70
Water penetration			
@ 28 days (mm)	25.0	6.0	1.5
Rapid Chloride Penetration			
@ 28 days (Coulombs)	2641	1763	712

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The results show that the compressive strength of the concrete modified with 5-10% of the particular waterproofing additive can be maintained or increased by up to 4% and 10% at 28 days and 56 days respectively. The water permeability, water absorption and chloride permeability are drastically reduced. Even at a water/cement ratio of 0.45 and an addition of 5% modified silica fume, the water penetration was only 6 mm, which is far below the 20 mm (average) penetration as specified in ENV206 for water impermeable concrete. The water absorption can also be controlled to below 1%.

Different waterproofing additives, or mixtures of additives, as described for example 1 could be used in preparing concrete as for this example.

EXAMPLE 3 - Water Sorptivity of Concrete

One of the additional benefits of the novel waterproofing additives described above is the reduced water sorptivity of the modified concrete. The sorptivity test is in fact similar to the surface water absorption test. The only difference is that the specimen in this case is not fully immersed in water, instead only the bottom face of the test specimen is placed in contact with water. In this way capillary suction can be directly visually monitored by observing the height increase of the wetted areas, or by measurement of the weight gain. The following example demonstrates the sorptivity behaviour of the concrete under capillary forces.

The concrete mixture proportions used for the test were the same as given in example 2 with 10% addition of modified silica fume. Additionally, a concrete with 10% unmodified silica fume was prepared for comparison. The concrete was cured for 28 days and core samples having dimensions of 75 mm in diameter and 75 mm in height were taken. The samples were coated with an epoxy resin over the length of the longitudinal faces and were dried in an oven at 105°C for 3 days and cooled in a desiccator for 1 day before the test. The test specimen was placed in contact with water at the bottom surface of the cylinder and the weight gain of the specimen was measured after 30 and 60 minutes and 24 hours of water contact. The specimens were split into two halves after 24 hours and the height of the wetted

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areas were measured. The results are shown in table 10.

Table 10: Comparison of Water Sorptivity of Plain Concrete, Silica Fume Concrete and Concrete with Modified Silica Fume

Concrete W/C Ratio	Plain		SF-Concrete		MSF-Concrete	
	0.36	0.45	0.36	0.45	0.36	0.45
Weight gain (g)						
@ 30 min	2.5	4.2	1.9	3.9	0.4	1.0
@ 60 min	4.0	7.5	3.2	5.9	0.9	1.9
@ 24 hours	13.8	22.8	10.2	17.6	3.0	5.1
Height of wetted area						
@ 24 hours (mm)	51	63	38	48	4	10

It is evident that the sorptivity of silica fume concrete is still very high, due to the presence of fine capillary pores. The hydrophobically modified silica fume is highly effective in reducing the capillary suction of the concrete, which is highly beneficial for a durable concrete so as to prevent rising damp and formation of efflorescence, reduce the build up of chloride and sulfate concentrations at the tidal and splash zones of marine concrete, minimize freeze-thaw damage and reduce algal growth on the concrete's surface.

In summary, the improved waterproofing additives described above have been observed to provide an improved and economical solution to produce highly durable water impermeable and damp-proof concrete which is able to overcome the disadvantages of the relatively high water absorption of waterproofed concrete containing silica fume and the reduced compressive strength, relatively high water permeability of waterproofed concrete containing hydrophobic compounds. It was found that waterproofing concrete can be produced with the addition of a modified pozzolanic composition to meet the water impermeability of concrete as specified in

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ENV 206 and the water absorption of less than 1% tested in accordance with BS1881 : Part 122.

As described in the examples above, pozzolanic materials are used as carriers for the hydrophobic compounds and therefore a pre-emulsifying is not necessary, providing a substantial advantage over the prior art. The pozzolan appears to act as a reactive pore filler by reacting with the hydration products of the cement to form insoluble precipitants which reduce the porosity and the pore size of the cement paste. At the same time the absorbed hydrophobic compound is believed to migrate toward the air/water interface of the concrete and form a hydrophobic layer at the concrete surface and the walls of the capillary pores which form an effective barrier against capillary suction of water. The novel waterproofing additives described above have been found to provide a highly advantageous solution for providing concrete with both water impermeable and damp-proof characteristics. The use of such waterproofing additives is very straightforward and does not differ from the normal use of silica fume in concrete production. In fact, the workability of fresh concrete containing the said novel waterproofing additive has been found to be better than the normal silica fume concrete, as the hydrophobic compounds act as an internal lubricant for the cement particles.

The present invention may include any feature or combination of features disclosed herein either implicitly or explicitly or any generalisation thereof irrespective of whether it relates to the presently claimed invention. In view of the foregoing description it will be evident to a person skilled in the art that various modifications may be made within the scope of the invention.

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CLAIMS

1. A waterproofing additive for cement and/or concrete, comprising at least one pozzolanic material modified with at least one hydrophobic material.
2. A waterproofing additive as claimed in claim 1, wherein the pozzolanic material comprises one or more of silica fume, microsilica and metakaolin.
3. A waterproofing additive as claimed in claim 2, wherein the pozzolanic material comprises silica fume and microsilica.
4. A waterproofing additive as claimed in claim 3, wherein the pozzolanic material comprises approximately equal amounts of silica fume and microsilica by weight.
5. A waterproofing additive as claimed in any one of claims 2 to 4, wherein the silica fume is densified silica fume.
6. A waterproofing additive as claimed in any one of claims 2 to 5, wherein the microsilica is refined natural microsilica.
7. A waterproofing additive as claimed in any preceding claim, wherein the hydrophobic material is a metallic or organic soap of a paraffinic acid.
8. A waterproofing additive as claimed in any preceding claim, wherein the hydrophobic material is calcium stearate.
9. A waterproofing additive as claimed in any of claims 1 to 6, wherein the hydrophobic material is an ester of a paraffinic acid.
10. A waterproofing additive as claimed in any of claims 1 to 6, wherein the hydrophobic material is butyl stearate.

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11. A waterproofing additive as claimed in any of claims 1 to 6, wherein the hydrophobic material is oleic acid, a wax emulsion, siloxane or a silicon emulsion.
12. A waterproofing additive as claimed in any preceding claim, wherein the pozzolanic material is modified with at least two hydrophobic materials.
13. A waterproofing additive as claimed in any preceding claim, wherein the pozzolanic material is modified by spraying and/or blending with the hydrophobic material(s).
14. A waterproofing additive as claimed in any preceding claim, comprising from 5 to 30% of total hydrophobic material(s) by weight of the pozzolanic material.
15. A waterproofing additive as claimed in claim 14, comprising around 10% of total hydrophobic material(s) by weight of the pozzolanic material.
16. A cement mortar or concrete comprising a waterproofing additive as claimed in any preceding claim.
17. A cement mortar or concrete as claimed in claim 16, comprising from 5 to 15% of the pozzolanic material by weight of cement.
18. A cement mortar or concrete as claimed in claim 16 or 17, having a water absorption in accordance with BS1881 : Part 122 of less than 1%.
19. A method of preparing a waterproofing additive for cement and/or concrete, comprising modifying a pozzolanic material by spraying and/or blending with a hydrophobic material.
20. A method as claimed in claim 19, wherein the step of spraying and/or blending is performed using a high speed/shear mixer.
21. A method of preparing cement mortar or concrete comprising mixing

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cement, sand and water with a waterproofing additive as claimed in any of claims 1 to 15.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER

Int Cl⁶: C04B 22/06, 24/06, 111/27

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C04B 22/06, 24/06, 111/27

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
AU: IPC as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
WPAT

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Derwent Abstract Accession No: 81810Y/46, Class A93 E12 L02, JP,A, 52117925 (NAKAGAWAT) 3 October 1977	1, 7-10, 12, 13, 19
X	WO,A, 93/04007 (BORAL AUSTRALIAN GYPSUM LIMITED) 4 March 1993	1, 11, 15-17, 21
X	US,A, 5472501 (DASTOL) 5 December 1995	1, 2, 16, 21
X	US,A, 4310486 (CORNWELL) 12 January 1982	1, 2, 16, 21
X	EP,A, 393681 (TECHNICHE INDUSTRIALI) 24 October 1990	1, 16, 21

☐ Further documents are listed in the continuation of Box C

☒ See patent family annex

* Special categories of cited documents:

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Date of the actual completion of the international search
20 March 1998

Date of mailing of the international search report
31 MAR 1998

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No.
PCT/SG 97/00064

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report				Patent Family Member			
WO	93/04007	AU	23857/92	EP	599872	NZ	243913
US	5472501	US	5275652	AT	4276/83	AU	22159/83
		BE	898398	BR	8306701	CA	1220793
		CH	658854	DD	212953	DE	3343948
		DK	5603/83	ES	527825	ES	8505904
		FI	834404	FR	2537127	GB	2131409
		IT	1167273	JP	59111963	MX	157587
		NL	8304193	NO	153566	NZ	2K06493
		PH	19938	PL	244938	PT	77741
		SE	8306700	ZA	8308678		
US	4310486	US	4088808	US	3995086	US	4036839
		US	4098755	US	4088804	US	4039170
EP	0393681	IT	1229844	PT	93816		
END OF ANNEX							